

COATINGS. ENAMELS

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GLASS ENAMEL COATINGS WITH ANTIBACTERIAL EFFECT FOR PROTECTING WATER-HEATERS

O. V. Shalygina,^{1,3} G. K. Voronov,^{1,4} and G. A. Loshko²

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The antibacterial effect of special glass enamel coatings developed to protect water heaters is evaluated. Coatings with an antibacterial agent are shown to be effective against the micro-organisms *E. Cloacae* and *E. Coli*.

Key words: glass enamel coating, micro-organism, antibacterial effect, low-carbon steel.

A great deal of attention is being given to glass enamel coatings with antibacterial properties. This concerns, first and foremost, coatings for household appliances and sanitary devices that come into contact with food products and drinking water. Of special interest is to impart antibacterial properties to protective coatings for the interior tanks of water heaters.

Some types of pathogenic micro-organisms, such as, *Enterobacter cloacae* and *Escherichia coli*, which form a biofilm which is a health hazard and resists ordinary disinfectants, develop on articles which are in contact with water for a long time [1].

Several methods of obtaining a bactericidal effect exist. They are used to eliminate or decrease the number of micro-organisms on the surface of a coating. These methods include the following: physical action (ordinary cleaning), thermal action (using hot air for dry-heating in a box or heating under pressure in an autoclave) as well as boiling or application of water vapor. These methods are quite effective, but they cannot always be implemented because of the large size of some enameled articles and equipment. In addition, micro-organisms can be eliminated by using high-energy radiation (UV, microwave or ionizing). Such methods are effective for disinfecting commercial equipment. The ena-

meled surfaces in a household are disinfected, as a rule, by means of chemicals containing strong oxidizers based on chlorine and sodium hydroxide, which require surfaces to be carefully washed after application. An alternative method of disinfection, which can be used for household appliances and equipment, is to introduce into the glass enamel coatings components that give a bactericidal effect.

Ordinarily, an antibacterial effect is achieved by introducing into glass enamel coatings silver compounds which can manifest bactericidal properties even at relatively low concentrations [2]. Silver is quite effective and safe, but at the same time it increases the cost of an article considerably, which is not always justifiable.

Some studies confirm the presence of antibacterial properties even for mixed-valence metal oxides, specifically, with respect to *E. Coli* and *S. aureus* [3, 4]. Their antibacterial action is based on the transfer of antibacterial factors (in the form of Me^{2+} cations) into a solution containing bacteria as well as on the oxidative effect with respect to an organic structural component of bacteria. This makes it possible to use them in glass enamel coatings as a bactericidal agent which is considerably less expensive than silver compounds.

To evaluate the effectiveness of such coatings compositions of glass enamels whose antibacterial properties are due to a complex bactericidal agent containing ZnO, CuO, MnO₂ and CoO were synthesized.

EXPERIMENTAL PART

The development of glass enamels for protecting the inner surface of steel tanks used in water heaters is based on

¹ National Technical University – Khar'kov Polytechnical Institute, Khar'kov, Ukraine.

² Sanitary-Epidemiological Office, Division of Medical Provision, General Administration of the Interior Ministry of Ukraine in Khar'kov Oblast', Khar'kov, Ukraine.

³ E-mail: shalygina oksana@ukr.net.

⁴ E-mail: voronov1976@ukr.net.

TABLE 1. Required Specifications for the Properties of Coatings for Water Heater Tanks

Property	Standard	Indicator	Remarks
Chemical resistance	DIN 4753/3	min class A	10% solution of HCl or citric acids, 1 h
Water resistance	DIN 4753/3	Mass loss max 3.5 g/m ²	Boiling 504 h; repeat 2 times
Thermal resistance	DIN 4753	Undamaged coating	3 cycles: 20, 200, 15°C; repeat 5 times
Impact strength	DIN 4753; ISO 4532	10 N	Fracture diameter ≤ 1.5 mm after 24 h
Physiological testing	DIN 4753	Aqueous extract from enamel must not contain lead and cadmium	
Coating thickness	DIN 4753		0.15 – 0.50 mm
Firing temperature			840 – 860°C

the results of previous studies performed by a team at the Laboratory of Glass and Enamels at the National Technical University – Khar'kov Polytechnic University. The working properties of glass-enamel coatings are determined by the properties of the initial frit or mixture of several frits and must correlate to the specifications developed for certain types of products. The specifications for the properties of protective glass enamel coatings for the inner steel tanks of water heaters (Table 1) are regulated by international standards, specifically, European norms DIN 4753/3 [5].

The Bn series of compositions of glass enamel frits was developed to obtain primer-free protective coatings on the interior steel tanks for water heaters, matching the complex of working specifications, presented in Table 1, for this type of article. The alkali-boron-aluminum-silicate system $R_2O-RO-B_2O_3-Al_2O_3-SiO_2$ was used as the base for the glass enamels. In addition, titanium and zirconium oxides added to the glass-enamel frit secure the required chemical and water resistance indicators of the coatings. The bonding strength of the single-layer no-undercoat protective coating with a steel base (substrate) was obtained by introducing a complex catalyst to activate the bonding of the complex composition [6].

The antibacterial effect of the new series Bn glass-enamel coatings, containing a complex bactericidal agent with respect to the bacteria *Enterobacter Cloacae* and *Escherichia Coli*. For comparison, typical enamel used to protect the interior tanks of heat heaters was also studied.

Both types of enamels were deposited on 50 × 50 mm steel samples made of low-carbon steel. The coatings were fired in an electric laboratory furnace at temperature 840 – 860°C. The thickness of the coatings was 150 – 200 μm.

The antibacterial action of the coatings was evaluated using the international technical norms of the ISO 22196:2007 standard. This standard describes a method for evaluating the antibacterial activity but does not regulate its value. The results of matching or not matching with respect to antibacterial activity are judged by agreement between the producer and user.

Following protocol a bacterial suspension was deposited on the experimental and control samples, which were placed in Petri dishes. Inocula of *E. Cloacae* and *E. Coli* with concentration 10⁶ CFU/ml were used for the experiment. The samples were kept at temperature 37°C for 24 h. The studies were performed at least five times for each type of coating in order to confirm the validity of the results.

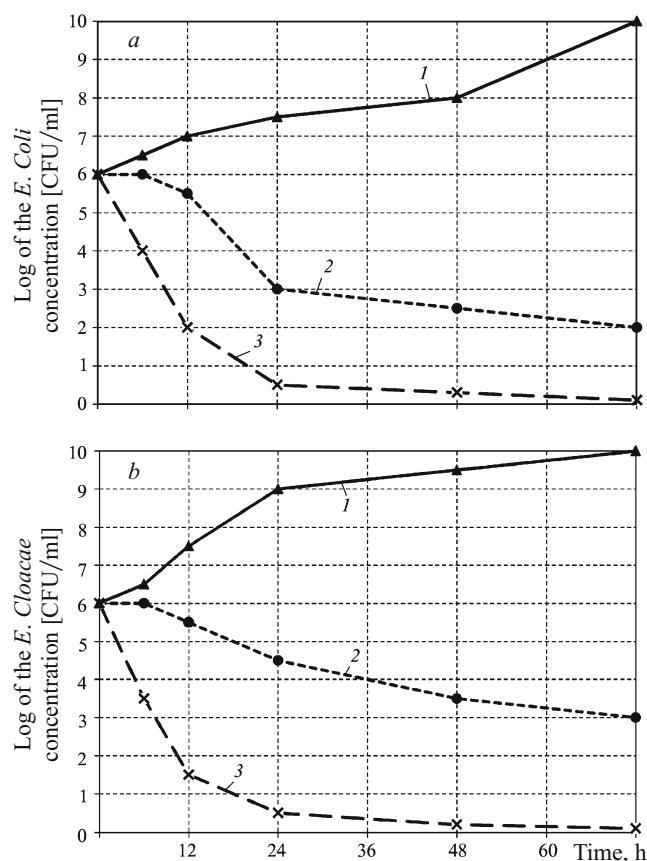


Fig. 1. Character of the change in the concentration of colony-forming units of *E. Coli* (a) and *E. Cloacae* (b): 1) control sample; 2) typical glass-enamel coating; 3) Bn glass-enamel coating, containing a complex bactericidal agent.

The intensity of bacterial growth after thermostating was evaluated visually by sowing onto Endo medium according to the number of colony-forming units (CFU) after 6, 12, 24, 48 and 72 h of thermostatic soaking. The character of bacterial growth for coating samples with and without a bactericidal agent as compared with the control sample is as follows.

Strong growth of both types of bacteria is observed in the control sample. For the sample coated with typical enamel, the initial *E. Coli* concentration decreases appreciably after thermostating and the *E. Cloacae* concentration decreases very little. For the sample with the series Bn coating, containing a complex bactericidal agent, a sharp decrease of the initial concentration of bacteria was observed in both cases. The results for the change of the concentration of colony-forming units with long-time thermostating are presented in Fig. 1.

A distinct bactericidal effect of the Bn series coating with thermostating for 24 h was observed. This is due to the activity of the constituent substances of the bactericidal agent, which act on the bacteria cells by means of oxidation of their structural proteins and enzymes, which makes them poisonous for entero-bacteria.

CONCLUSIONS

On the one hand, the results of this work make it possible to conclude that the new glass-enamel coatings with complex

filler that is bactericidal with respect to entero-bacteria exhibit an antibacterial effect. On the other hand, it can be stated that the new coatings manifest new functional properties and new antibacterial agents should be sought and their properties studied.

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